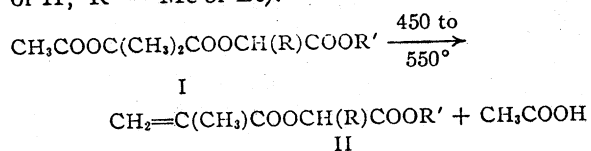


Preparation of α -Carbalkoxyalkyl Methacrylates by Pyrolysis of the Corresponding α -Acetoxyisobutyrate

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In an earlier paper² it was demonstrated that α -carbalkoxyalkyl methacrylates³ (II) can be made in satisfactory yields by pyrolyzing the corresponding α -acetoxyisobutyrate (I, R = Me or H; R' = Me or Et).



The present paper records results obtained in a further study of the pyrolysis method of preparing methacrylates (II). The additional esters made pyrolytically are the methacrylates of allyl glycolate and of allyl, methallyl, tetrahydrofurfuryl, benzyl and β -chloroethoxyethyl lactates.

(1) One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, United States Department of Agriculture. Article not copyrighted.

(2) E. M. Filachione, J. H. Lengel and C. H. Fisher, *This Journal*, **68**, 330 (1946).

(3) C. E. Rehberg, M. B. Dixon and C. H. Fisher, *ibid.*, **67**, 208 (1945); I. E. Muskat and F. Strain, U. S. Patent 2,384,119, Sept. 4, 1945.

The α -acetoxyisobutyrate (I) used in the pyrolysis experiments were prepared in high yields by treating allyl glycolate and several lactic esters (allyl, methallyl, tetrahydrofurfuryl, benzyl and β -chloroethoxyethyl) with α -acetoxyisobutyryl chloride. The resulting acetoxyisobutyrate (Table I) were decomposed by passage through a Pyrex glass tube heated at about 450° (Table II).

Although the esters (I) pyrolyzed had three esterified carboxyl groups, decomposition occurred preferentially at the acetate group, the principal products being acetic acid and the corresponding methacrylates (II, yields, 65–85%). On the basis of these and earlier² findings, it is concluded that the pyrolysis method is generally useful for the preparation of methacrylates (II) of alkyl glycolates and lactates. Presumably the method is useful also for preparing esters (II) in which R is ethyl or higher, but less suitable for esters (II) in which R' is a secondary or tertiary alkyl group. It is anticipated that only relatively low yields of carbalkoxyisopropyl methacrylates ($\text{CH}_2=\text{C}(\text{CH}_3)\text{COOC}(\text{CH}_3)_2\text{COOR}$) would be obtained in the pyrolysis of $\text{CH}_3\text{COOC}(\text{CH}_3)_2\text{COOC}(\text{CH}_3)_2\text{COOR}$,

TABLE I
PREPARATION AND PROPERTIES OF ACYLATED HYDROXY ESTERS

| α -Acetoxyisobutyrate of | Yield, % of theoretical | B. p. °C. | Mm. | d_{20}^4 | n_D^{20} | Mol. refraction Calcd. | Found | Sapon. equiv. Calcd. | Found | Carbon, % Calcd. | Found | Hydrogen, % Calcd. | Found |
|------------------------------------|-------------------------|-----------|------|------------|------------|------------------------|-------|----------------------|-------|------------------|--------------------|--------------------|-------|
| Allyl lactate | 89 | 82 | 0.2 | 1.0864 | 1.4357 | 62.11 | 62.11 | 86.1 | 86.8 | 55.80 | 55.41 | 7.02 | 7.04 |
| Methallyl lactate | 81 | 82-85 | 0.1 | 1.0713 | 1.4381 | 66.73 | 66.73 | 90.8 | 91.2 | 57.34 | 57.59 ^a | .. | .. |
| Allyl glycolate | 79 | 84-86 | 0.25 | 1.1224 | 1.4407 | 57.49 | 57.43 | 81.41 | 81.55 | 54.09 | 54.27 ^a | .. | .. |
| Tetrahydrofurfuryl lactate | 87 | 145 | 1.5 | 1.1347 | 1.4475 | 71.26 | 71.29 | | | 55.62 | 55.59 | 7.33 | 7.32 |
| Benzyl lactate | 86 | 136 | 0.6 | 1.1285 | 1.4812 | 77.45 | 77.77 | 102.8 | 102.7 | 62.32 | 62.05 | 6.54 | 6.53 |
| β -Chloroethoxyethyl lactate | 75 | 145 | 0.2 | 1.1798 | 1.4478 | 73.71 | 73.66 | | | 48.07 | 47.91 | 6.52 | 6.59 |

^a By wet oxidation (D. D. Van Slyke and J. Folch, *J. Biol. Chem.*, 136, 509 (1940)).

TABLE II
PYROLYSIS OF ACETYLATED HYDROXY ESTERS

| Ester pyrolyzed, g. Acetoxyisobutyrate of | Temp., °C. | Feed rate, g./min. | Contact time, sec. | Ester decomposed, % | Methacrylate Boiling range, °C. | Press., mm. | Yields, ^a mole per mole of ester destroyed | Acetic acid Titr. | Dist. | Acetone |
|---|------------|--------------------|--------------------|---------------------|---------------------------------|-------------|---|-------------------|-------|---------|
| Allyl lactate, 147 | 446 | 2.0 | 10.1 | 79 | 54-62 | 0.45 | 0.82 | 0.92 | 0.76 | .. |
| Methallyl lactate, 346 | 450 | 2.8 | 7.5 | 63 | 53-60 | .2 | .85 | .97 | .84 | 0.07 |
| Allyl glycolate, 130 | 450 | 2.4 | 7.9 | 69 | 51-62 | .35 | .78 | .96 | .84 | .. |
| Tetrahydrofurfuryl lactate, 288 | 450 | 2.3 | 10.1 | 68 | 83-91 ^b | .1 | .65 | .93 | .80 | .08 |
| Benzyl lactate, 159 | 450 | 2.4 | 9.9 | 65 | 97-104 ^c | .2 | .71 | .92 | .72 | .07 |
| β -Chloroethoxyethyl lactate, 114 | 450 | 2.7 | 9.5 | 66 | 104-116 ^d | .25 | .79 | .88 | .66 | .04 |

^a Methacrylate yield based on that obtained in first distillation; acetic acid yield based on that obtained in redistillation. ^b Much polymerization occurred during distillation. ^c Hydroquinone distilled with the monomer. ^d Phenyl- β -naphthylamine used as inhibitor.

TABLE III
PROPERTIES OF MONOMERIC α -CARBALKOXYLALKYL METHACRYLATES

| Methacrylate of | °C. | B. p. Mm. | d_{20}^4 | n_D^{20} | Mol. refraction Calcd. | Found | Sapon. equiv. Calcd. | Found | C, % Calcd. | Found ^a |
|---|---------|-----------|------------|------------|------------------------|-------|----------------------|-------|-------------|--------------------|
| Allyl lactate | 52-53 | 0.15 | 1.0352 | 1.4452 | 50.75 | 50.98 | 99.10 | 99.15 | 60.59 | 60.63 |
| Methallyl lactate | 57-59 | 0.25-0.30 | 1.0160 | 1.4475 | 55.37 | 55.90 | 106.1 | 106.6 | 62.24 | 61.93 |
| | 66 | 0.55 | | | | | | | | |
| Allyl glycolate | 73-74 | 1.0 | 1.0760 | 1.4513 | 46.14 | 46.12 | 92.09 | 92.66 | 58.69 | 58.39 |
| | 53-54 | 0.3 | | | | | | | | |
| Tetrahydrofurfuryl lactate | 91-95 | 0.15-0.20 | 1.1015 | 1.4586 | 59.94 | 60.08 | 121.1 | 120.5 | 59.49 | 59.53 |
| | 109-110 | 0.7 | | | | | | | | |
| Benzyl lactate | 92-95 | 0.1 | 1.0975 | 1.5002 | 66.09 | 66.53 | 124.1 | 118.8 | 67.72 | 67.68 |
| | 96-101 | 0.2 | | | | | | | | |
| β -Chloroethoxyethyl lactate ^b | 97-99 | 0.15 | 1.1528 | 1.4579 | 62.35 | 62.64 | | | ... | ... |

^a By wet oxidation (D. D. Van Slyke and J. Folch, *J. Biol. Chem.*, 136, 509 (1940)). ^b Chlorine content, 13.36% (theoretical, 13.40%).

a more probable decomposition product⁴ being $\text{CH}_2=\text{C}(\text{CH}_3)\text{COOR}$.

The methacrylates (Table III) were mass polymerized at 60 to 65° in the presence of a small quantity (0.1 to 0.15%) of benzoyl peroxide. With the exception of the β -chloroethoxyethyl ester (a soft, flexible, amber polymer that became brittle at approximately -5°), all the polymeric methacrylates were hard at room temperature and virtually colorless. The polymeric benzyl and tetrahydrofurfuryl esters became soft at approximately

(4) This assumption is based on the pyrolysis behavior³ of $\text{CH}_3\text{COOCH}(\text{CH}_3)\text{COOCH}(\text{CH}_3)\text{COOCH}_3$, which yields methyl acrylate as the principal product.

45° and 35°, respectively. Presumably the polymeric allyl and methallyl esters, insoluble and infusible, were cross-linked.

The authors are indebted to Frances J. Cooper, Mary J. Welsh and C. L. Ogg for the saponification equivalents and ultimate analyses and to W. P. Ratchford and E. J. Schaeffer for pyrolyzing the acetoxyisobutyrate.

Experimental

Allyl Glycolate.—Water was distilled from a mixture of 210 g. of technical-grade glycolic acid (72.4% concentration) and 0.5 ml. of concentrated sulfuric acid for three hours at 100° and 20 to 30 mm. pressure. The resulting

residue (123 g. of polyglycolic acid having an equivalent weight on titration of 64.75; *i. e.*, 117.5% by weight as glycolic acid) was semi-solid.

A mixture of 32.4 g. of the polyglycolic acid (equivalent to 0.5 mole of glycolic acid and containing 0.13 ml. of sulfuric acid) and 2.5 moles of allyl alcohol was heated in a bomb (glass liner) for six hours at 120–139°. Anhydrous sodium acetate (0.6 g.) was added to the reaction mixture and the mixture was distilled to separate allyl glycolate (66% yield; b. p. 60–72° (8 mm.); d_{20}^{20} , 1.0901; n_D^{20} 1.4418; M^{20}_D 28.09 (calculated, 28.00); saponification equiv., 122.5 (calculated, 116.1)). Muskat and Strain⁶ prepared allyl glycolate but did not describe it.

Allyl Lactate.—This compound, previously described,^{6,7,8} was prepared by the reaction of allyl alcohol with condensation products of glycerol and lactic acid. Water (116 g.) was distilled through a Vigreux column from a mixture of 81.7% edible-grade lactic acid (equivalent to 3 moles), 1 mole of glycerol and 0.75 ml. concentrated sulfuric acid for three hours. This was accomplished by heating the mixture on a water-bath while the system was at a pressure of 40–50 mm. The pale yellow, viscous residue (307 g.) had a saponification equivalent, including free acidity, of 101.4 (glyceryl trilactate, 102.7). A mixture of 50.5 g. of the glycerol-lactic acid product (equivalent to 0.5 mole of lactic acid) and 2.5 moles of allyl alcohol was heated in a bomb (glass liner) for two hours at 120–30°. The reaction mixture was treated with 0.5 g. of anhydrous sodium acetate and distilled in vacuum. Allyl lactate, b. p. 60–61° at 7 mm., n_D^{20} 1.4363, was isolated in 73% yield.

Benzyl Lactate.—A mixture of 1 mole of methyl lactate, 4 moles of benzyl alcohol and 1 g. of aluminum isopropoxide was heated under a Vigreux column fitted with a variable take-off distilling head, methanol being distilled as formed (temperature of the reaction mixture increased gradually from 170 to 192°, and 36 ml. of distillate was collected during four to five hours). The reaction mixture was then distilled under reduced pressure. The yield of benzyl lactate, b. p. 103–104° at 1.3 mm., was 82%. The refractive indices, n_D^{20} , of two different preparations were 1.5143 and 1.5155. This compound has been made by the alcoholysis of ethyl lactate⁹ and by the interaction of benzyl chloride and sodium lactate.¹⁰

Methallyl lactate was prepared by direct esterification of lactic acid with methallyl alcohol, some modifications of the previously reported method⁶ being incorporated. A mixture of 110 g. of 81.7% of edible lactic acid, containing 1.0 mole of available lactic acid and 216 g. (3.0 moles) of methallyl alcohol, was refluxed and the vapors were led through a Vigreux column to a Barrett-type Dean-and-Stark moisture trap. The receiver of the moisture trap was jacketed and cooled by circulating cold water. After approximately seven hours removal of water virtually ceased, and 37 ml. of aqueous layer was collected. The reaction mixture was then distilled. There was obtained 86 g., or 60% of the theoretical amount of methallyl lactate, b. p. 85–90° at 15 mm., n_D^{20} 1.4390.

Tetrahydrofurfuryl Lactate was prepared essentially as described previously^{11,12} by alcoholysis of methyl lactate.

(5) I. E. Muskat and F. Strain, U. S. Patent 2,370,574, Feb. 27, 1945.

(6) C. H. Fisher, C. E. Rehberg and Lee T. Smith, *THIS JOURNAL*, **65**, 763 (1943); C. E. Rehberg and C. H. Fisher, U. S. Patent 2,367,798.

(7) C. E. Rehberg and C. H. Fisher, *J. Org. Chem.*, **12**, 226 (1947).

(8) I. E. Muskat and F. Strain, U. S. Patent 2,364,126, Sept. 4, 1945.

(9) R. Burns, D. T. Jones and P. D. Ritchie, *J. Chem. Soc.*, 400 (1935).

(10) M. Gomberg and C. C. Buehler, *THIS JOURNAL*, **42**, 2059 (1920).

(11) H. V. Claborn, U. S. Patent 2,223,363, Nov. 19, 1940; U. S. Patent 2,229,997, Jan. 28, 1941.

(12) M. L. Fein, W. P. Ratchford and C. H. Fisher, *THIS JOURNAL*, **66**, 1201 (1944).

The alcoholysis, however, was carried out in the absence of a catalyst. By refluxing a mixture of 10 moles of methyl lactate and 30 moles of tetrahydrofurfuryl alcohol with the continuous removal of methanol, an 85% yield of tetrahydrofurfuryl lactate was obtained; b. p. 84–86° at 0.1 mm., n_D^{20} 1.4571, d_{20}^{20} 1.1360.

β -Chloroethoxyethyl Lactate.—Direct esterification of β -chloroethoxyethanol (diglycol chlorohydrin) with lactic acid, as previously described,¹³ was used to obtain this ester, b. p. 91° at approximately 0.1 mm., n_D^{20} 1.4567.

α -Carbalkoxyalkyl α -Acetoxyisobutyrate.—Acetoxyisobutyryl chloride was prepared and used to acylate the hydroxy esters as previously described.² Physical properties of the acyl derivatives (obtained in 80 to 90% yields) are recorded in Table I.

Pyrolysis.—In general the previous procedure was followed.² The acylated hydroxy esters were pumped¹⁴ to the top of a vertical Pyrex glass tube (25 mm. diameter) heated electrically over a length of 33 cm. The thermocouple was located 10 cm. from the bottom of the heated zone. The pyrolysis tube was packed with short lengths of Pyrex glass tubing, and the free space of the heated zone was 78 ml.

The pyrolyzates, containing hydroquinone, were distilled in a 56-cm. Vigreux column in an atmosphere of carbon dioxide (Table II). The acetic acid fraction was collected at water pump pressure (in a solid carbon dioxide trap), whereas the methacrylates and undecomposed esters were isolated at pressures below 1 mm.

The constants of the methacrylates (Table III) were obtained on redistilled fractions. The methacrylates of tetrahydrofurfuryl lactate, benzyl lactate and chloroethoxyethyl lactate partly polymerized during distillation, resulting in losses.

Solubilities of the Polymeric Carbalkoxyethyl Methacrylates.—The polymeric methacrylates (0.1 g.) were allowed to stand at room temperature with approximately 1 ml. of solvent. The polymethacrylate of tetrahydrofurfuryl lactate swelled in toluene, benzene, ethylene dichloride, nitromethane, dioxane, acetone, methyl lactate and ethyl acetate. The polymethacrylate of benzyl lactate was soluble in nitromethane and partly soluble in toluene, benzene, ethylene dichloride, dioxane, acetone, methyl lactate and ethyl acetate. The polymethacrylate of β -chloroethoxyethyl lactate was soluble in toluene, benzene, ethylene chloride, nitromethane, dioxane, acetone, methyl lactate, and ethyl acetate. The polymers listed above were insoluble in heptane and ethanol, but dissolved slowly at room temperature in 10% sodium hydroxide. The polymers after swelling by acetone dissolved much more rapidly in the sodium hydroxide, presumably by saponification of the esterified lactic acid carboxyl group.

Summary

The method of producing α -carbalkoxyalkyl methacrylates ($\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCHR}\text{COOR}'$; $\text{R} = \text{H}$ or Me) by pyrolysis of the corresponding α -acetoxyisobutyrate ($\text{CH}_3\text{COOC}(\text{CH}_3)_2\text{COOCHR}\text{COOR}'$) was used satisfactorily to prepare the methacrylates of allyl glycolate and of allyl, methallyl, benzyl, tetrahydrofurfuryl, and β -chloroethoxyethyl lactates. It is concluded that the pyrolytic method is generally useful for making α -carbalkoxyalkyl methacrylates.

The methacrylates polymerized readily when heated in the presence of benzoyl peroxide. The polymeric methacrylate of β -chloroethoxyethyl lactate was amber and flexible, the allyl and

(13) M. L. Fein and C. H. Fisher, *ibid.*, **63**, 2631 (1946).

(14) B. B. Corson and W. J. Cervený, *Ind. Eng. Chem., Anal. Ed.*, **14**, 899 (1942).

methallyl polymers were hard, colorless, insoluble and infusible and the benzyl and tetra-

hydrofurfuryl polymers were hard and colorless.
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